Europäisches Patentamt

(19) European Patent Office

Office européen des brevets

(11) **EP 1 143 023 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
10.10.2001 Bulletin 2001/41

(51) Int Cl.7: **C22C 38/00, C21C 7/00**

(86) International application number:
PCT/JP00/07091

(21) Application number: 00966448.3

(22) Date of filing: 12.10.2000

(87) International publication number:
WO 01/27342 (19.04.2001 Gazette 2001/16)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 12.10.1999 JP 28941299

(71) Applicant: **Nippon Steel Corporation**
Tokyo 100-8071 (JP)

(72) Inventors:
• UEMORI, Ryuji,
Nippon Steel Corporation Technical
Futtsu City, Chhiba 293-0011 (JP)

• TOMITA, Yukio,
Nippon Steel Corporation Technical
Futtsu City, Chhiba 293-0011 (JP)

• HARA, Takuya,
Nippon Steel Corporation Technical
Futtsu City, Chhiba 293-0011 (JP)

• AIHARA, Shuji,
Nippon Steel Corporation Technical
Futtsu City, Chhiba 293-0011 (JP)

• SAITOH, Naoki, Nippon Steel Corporation
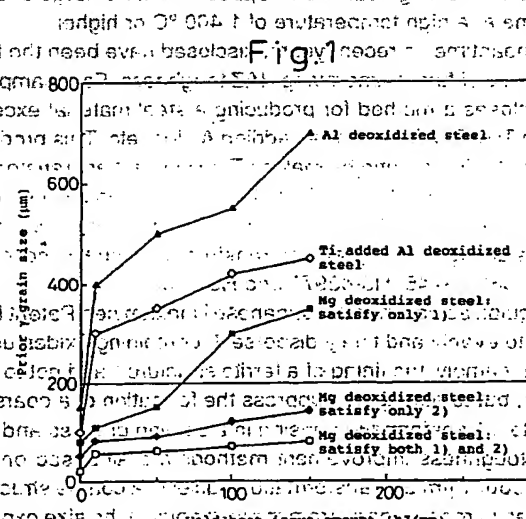Tokai City, Aichi 476-8686 (JP)

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
81675 München (DE)

(54) **STEEL FOR WELDED STRUCTURE PURPOSE EXHIBITING NO DEPENDENCE OF HAZ TOUGHNESS ON HEAT INPUT AND METHOD FOR PRODUCING THE SAME**

(57) The present invention relates to a steel for a welded structure with excellent HAZ toughness, containing, in terms of wt%, C: 0.01 to 0.2%, Si: 0.02 to 0.5%, Mn: 0.3 to 2%, P: 0.03% or less, S: 0.0001 to 0.03%, Al: 0.0005 to 0.05%, Ti: 0.003 to 0.05%, Mg: 0.0001 to 0.01% and O: 0.0001 to 0.008%, with the balance consisting of Fe and unavoidable impurities; and having particles dispersed in the steel at an average particle interval of 30 to 100 μm, the particles being formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle sizes of 0.2 to 5 μm as their nuclei, or particles dispersed in the steel at an average particle interval of 30 μm or less, the particles being formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle sizes of 0.005 to less than 0.2 μm as their nuclei.

Description

Technical Field

[0001] The present invention relates to a steel, for a welded structure, used for an offshore structure, a line pipe for transporting natural gas or crude oil, in architecture, in shipbuilding, for a bridge, for construction equipment or the like, and a method for producing the same. More specifically, the present invention relates to a steel, for a welded structure, requiring toughness at a weld zone, having a small prior austenite grain size at a weld heat-affected zone (hereunder referred to as "HAZ") even when the steel is welded on a heat input condition that the heat input during welding widely ranges from 0.5 kJ/mm to over 150 kJ/mm, and being excellent in toughness at the weld heat-affected zone (hereunder referred to as "HAZ toughness") without depending on the heat input condition.

Background Art

[0002] From the viewpoint of preventing the brittle fracture of a welded structure such as an offshore structure or the like, studies for suppressing brittle fracture arising at a weld zone, namely, many studies related to enhancing the HAZ toughness of a used steel plate, have been reported. In recent years, for improving welding procedure efficiency, ultra-large heat input welding (20 to 150 kJ/mm) having larger weld heat input than the formerly employed large heat input welding (about 20 kJ/mm or less) has been increasingly employed.

[0003] The difference between the influence of large heat input welding on a steel plate and that of ultra-large heat input welding on a steel plate is caused by the difference of their retention times at high temperatures of 1,400°C or more.

[0004] That is, since a retention time is extremely long in case of ultra-large heat input welding, the area where a crystal grain size markedly coarsens expands at a HAZ and toughness deteriorates considerably.

[0005] Generally, as measures for preventing the coarsening of crystal grains at a HAZ of a steel plate, known are the means to make use of the effect of pinning (a pinning effect) prior austenite grains (hereunder referred to as "prior γ grains," and the size thereof being referred to as a "prior γ grain size") by inclusion particles finely dispersed in the steel, the inclusion particles being, for example, TiN described in Japanese Unexamined Patent Publication No. S55-26164 or ZrN in "a steel for a large heat input welded structure characterized by containing, in weight %, 0.01 to 0.2% of C, 0.002 to 1.5% of Si, 0.5 to 2.5% of Mn, 0.002 to 0.1% of Ti and/or Zr, 0.004% or less of Ca and/or Mg, 0.001 to 0.1% of Ce and/or La, 0.005 to 0.1% of Al and 0.002 to 0.015% of N" as described in Japanese Unexamined Patent Publication No. S52-17314.

[0006] However, though such nitrides contribute to fining crystal grains by showing a pinning effect of pinning prior γ grains without dissolving in case of small or medium heat input welding, there is a problem that the nitrides easily dissolve in a steel by welding heat and disappear in case of large or ultra-large heat input welding having an extremely long retention time at a high temperature of 1,400 °C or higher.

[0007] In the meantime, in recent years, disclosed have been the technologies of using oxides generated in molten steel for the purpose of further improving HAZ toughness. For example, Japanese Unexamined Patent Publication No. S59-190313 discloses a method for producing a steel material excellent in weldability, characterized by deoxidizing molten steel with Ti or Ti alloy and then adding Al, Mg, etc. This production method is a technology to make use of the effect of increasing a ferrite ratio by making Ti oxides act as transformation nuclei of ferrite and to attempt to improve HAZ toughness by a method different from the former method of utilizing a pinning effect by precipitates such as nitrides.

[0008] After that, in this technical field, various inventions, including the inventions of attempting to increase the number of oxides acting as intragranular transformation nuclei, have been disclosed in Japanese Unexamined Patent Publication Nos. S61-79745, H5-43977 and H6-37364.

[0009] In particular, as described in Japanese Unexamined Patent Publication No. S59-190313, the essence of those technologies is "to evenly and finely disperse Ti containing oxides usable for the formation of ferrite nuclei during γ to α transformation, namely, the fining of a ferrite structure," and not to secure a pinning effect by nitrides and the like as described above, but to attempt to suppress the formation of a coarse brittle structure by accelerating ferrite transformation during γ to α transformation arising in a cooling process and to attain the fining of a structure.

[0010] These toughness improvement methods are all based on the technology to disperse and utilize relatively large oxides of about 1 μm as transformation nuclei in a coarse structure for promoting ferrite transformation in grains.

[0011] However, in recent years, from the viewpoint of the size expansion and weight reduction of welded structures, high tensile steels with higher strength are increasingly required and the addition amounts of alloying elements tend to increase in the chemical composition of the high strength steels. In this case, the existing HAZ toughness improvement measures to utilize ferrite transformation have been losing their effectiveness because of the increase of hardenability at a HAZ.

[0012] From the above viewpoints, to radically improve HAZ toughness, the pinning effect on prior γ grains can be expected on wide-ranging heat input conditions, and oxide particles can be soluble at a high temperature, like finely

dispersed nitrides in a steel. Moreover, in this case, it is considered that, if it is possible to obtain a transformation capability better than existing ferrite transformation nuclei, the HAZ toughness of a steel material used in this technical field will improve greatly.

[0013] As a method to introduce oxides, there is a method to add a deoxidizing element such as Ti, etc. alone in a refining process of steel. However, in many cases, the aggregations of oxides are formed during the holding of molten steel, resulting in the formation of coarse oxides, and the cleanliness of the steel rather deteriorates and thus toughness also deteriorates. To cope with that, as explained above, various contrivances for fining those oxides, including a complex deoxidizing method, have been implemented.

[0014] However, by the methods presently known, it is impossible to disperse, in steel, fine oxides having a function sufficient to perfectly prevent the coarsening of crystal grains in the case of large weld heat input.

Disclosure of the Invention

[0015] The object of the present invention is to provide a steel for a welded structure, excellent in HAZ toughness even if the steel is welded on any heat input condition, including ultra-large heat input, by improving the existing complex deoxidizing method, dispersing oxides and/or nitrides more finely and evenly than before, and further imposing, in addition, a ferrite transformation capability on the finely dispersed particles.

[0016] The gist of the present invention is as follows:

[0017] (1) A steel for a welded structure with HAZ toughness not susceptible to heat input, characterized by containing, in terms of wt%,

C: 0.01 to 0.2%,
Si: 0.02 to 0.5%,
Mn: 0.3 to 2%,
P: 0.03% or less,
S: 0.0001 to 0.03%,
Al: 0.0005 to 0.05%,
Ti: 0.003 to 0.05%,
Mg: 0.0001 to 0.01%, and
O: 0.0001 to 0.008%

with the balance consisting of Fe and unavoidable impurities;

and having particles dispersed in the steel at an average particle interval of 30 to 100 μm, the particles being formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle sizes of 0.2 to 5 μm as their nuclei, or particles dispersed in the steel at an average particle interval of 30 μm or less, the particles being formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle sizes of 0.005 to less than 0.2 μm as their nuclei.

[0018] (2) A steel for a welded structure with HAZ toughness not susceptible to heat input according to the item (1), characterized by further containing, in terms of wt%, one or more of

Cu: 0.05 to 1.5%,
Ni: 0.05 to 5%,
Cr: 0.02 to 1.5%,
Mo: 0.02 to 1.5%,
V: 0.01 to 0.1%,
Nb: 0.0001 to 0.2%,
Zr: 0.0001 to 0.05%,
Ta: 0.0001 to 0.05%, and
B: 0.0003 to 0.005%.

[0019] (3) A steel for a welded structure with HAZ toughness not susceptible to heat input according to the item (1) or (2), characterized by further containing, in terms of wt%, one or more of

Ca: 0.0005 to 0.005%, and
REM: 0.0005 to 0.005%.

[0020] (4) A steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of

the items (1) to (3), characterized by having the prior austenite grain sizes of 10 to 200 μm in its HAZ structure without depending on weld heat input.

[0021]　(5) A method for producing a steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of the items (1) to (4), characterized by: casting the steel in the state of adjusting the dissolved oxygen amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and a required amount of Mg successively or simultaneously after carrying out a weak deoxidation treatment by adding Si and Mn in a steelmaking process; or casting the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less.

[0022]　(6) A method for producing a steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of the items (1) to (4), characterized by: casting the steel in the state of adjusting the dissolved oxygen amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and required amounts of Al, Ca and Mg successively or simultaneously after carrying out a weak deoxidation treatment by adding Si and Mn at a steelmaking process; or casting the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less.

Brief Description of the Drawings

[0023]

Figure 1 is a graph showing prior γ grain sizes at HAZs when the amounts of weld heat input are varied.
Figure 2 is a schematic showing the forms of complex particles having ultra-fine Mg oxides as their nuclei.

Best Mode for Carrying Out the Invention

[0024]　It is known that Mg is an element to enhance the cleanliness of a steel by acting as a strong deoxidizer and a desulfurizing agent and thus to improve HAZ toughness.

[0025]　Further, as a means to improve HAZ toughness by controlling the dispersion of oxides, a technology of complex addition wherein Mg is added after Ti is added is disclosed in Japanese Unexamined Patent Publication No. S59-190313.

[0026]　However, as quoted before, the object of the technology is to accelerate a finely dispersion of the increase of Ti oxides, which are intragranular transformation nuclei, by adding Mg for pinning the oxides.

[0027]　The present inventors, paying their attention to the function of Mg as a strong deoxidizer, had the idea that a fine dispersion of oxides might be expected if the sequence and amount of the addition of the deoxidizer in a Ti added steel were controlled in a steelmaking process by making use of the characteristic of Mg which is more hardly caused aggregation and coarsening than Al.

[0028]　The present invention will hereunder be explained in detail.

[0029]　The present inventors systematically investigated the state of oxides when Mg was added to molten steel deoxidized weakly by adding Ti.

[0030]　As a result, it was found that oxides having two kinds of particle sizes were formed either when Ti and Mg were added in the order of Ti and then Mg or when Ti and Mg were added simultaneously and further, in the state of equilibrium, Mg was added again, after the molten steel was deoxidized by Si and Mn.

[0031]　Moreover, it was confirmed in the present invention that, in the first step Mg deoxidation, the same trends as stated above were also obtained when Al and Ca were added simultaneously or precedently.

[0032]　One kind is Mg containing oxides having grain sizes of 0.2 to 5.0 μm and the other kind is ultra-fine MgO or Mg containing oxides having grain sizes of 0.005 to 0.1 μm. It is thought that these oxides are formed based on the following reasons.

[0033]　Firstly, oxides, at the μm level composed of Ti or those mainly composed of Ti are once formed by the addition of Ti or the simultaneous addition of Ti and a small amount of Mg. Secondly, when Mg, which has strong deoxidizing ability, is further added in this state, the oxides already formed are reduced by Mg and Mg containing oxides at the μm level, mainly composed of Mg, are formed finally.

[0034]　Further, in this case, in spite of the amount of dissolved oxygen lowering, new fine oxides at the sub-μm level composed of Mg only are formed at the same time since the deoxidizing ability of Mg is stronger than that of Ti.

[0035]　As a result, an increase in the particle number and the fining of the particle size, which have not been obtained by a conventional adding method, can be realized.

[0036]　With regard to oxides having a size at the μm level, in general, the larger the number of oxides, having a size of 5 μm or more, is, the more the oxides tend to become the origins of fractures and, therefore, the upper limit of the Mg addition amount is regarded to be 30 to 50 ppm when Mg is added, as described in Japanese Unexamined Patent Publication No. H9-157787.

[0037]　However, in the present invention, the above problem can be avoided and Mg can be added up to 100 ppm.

[0038]　On the other hand, in case of the deoxidation by Ti or the deoxidation by Ti and a small amount of Mg, dissolved

EP 1 143 023 A1

oxygen still remains in the molten steel because the deoxidation is caused by a weak deoxidizing element or a small amount of a strong deoxidizing element. Therefore, when Mg is added again at that time, the oxidation reaction of Mg with not only the above-mentioned oxides at the µm level or sub-µm level but also the still remaining dissolved oxygen proceeds moderately and ultra-fine oxides form further. The reason why the ultra-fine oxides form is presumably that the clustering is suppressed due to the equation of the dissolved oxygen distribution in molten steel in addition to the reduction of the dissolved oxygen amount.

[0039] As explained above, the oxides formed in steel become the nucleus forming sites of sulfides and nitrides during casting, cooling thereafter or reheating in hot rolling processes.

[0040] Then, as a result of observing the state of the oxides in steel at a magnification of 1,000 to 100,000 times using an electron microscope, the states of the oxides existing in the steel can be arranged as described in items 1) and 2) below. Here, to observe the state of oxides existing in steel, it is preferable to observe 10 visual fields or more at a specified magnification (for example, about 100,000 times in case of ultra-fine oxides) and to measure the average particle interval.

1) Particles, which are formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle size of 0.2 to 5 µm as nuclei, are contained in steel at an average particle interval of 30 to 100 µm.

2) Particles, which are formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle size of 0.005 to less than 0.2 µm as nuclei, are contained in steel at an average particle interval of 30 µm or less.

[0041] The present invention relates to a steel material with excellent HAZ toughness obtained by the oxides existing in the state of the above items 1) and/or 2), and provides an epoch-making technology capable of extremely suppressing the toughness change at a HAZ, which largely depended on a heat input amount, formerly.

[0042] The improvement of HAZ toughness will further be explained hereunder.

[0043] As has been known so far, the higher the number of oxides is, and the more the sulfides and nitrides precipitate on the oxides, the more the intragranular transformation is accelerated. Since, as shown in the above item 1), the number of the particles increases over ten times compared with a conventional case and, with regard to complex precipitation too, 100 percent of sulfides or nitrides precipitate in combination, so far as it is confirmed, Mg contained oxides according to the present invention have an extremely large intragranular transformation ability.

[0044] Next, the fining of a prior γ particle size which is most important in the present invention will hereunder be explained based on Figure 1.

[0045] Figure 1 is a graph obtained by measuring the prior γ particle sizes at HAZs on each condition (1 kJ/mm, 10 kJ/mm, 50 kJ/mm, 100 kJ/mm or 150 kJ/mm) using 0.10C-1.0Mn steel as the base steel, taking the heat input amounts along the axis of the abscissas.

[0046] In case of actual joints, the prior γ particle size is obtained by taking the photographs (5 pictures or more), at a magnification of 50 to 200 times with an optical microscope, of microstructures obtained by extracting a part of a HAZ with cutting and processing, etc., applying polishing thereafter and further being subjected to Nitral corrosion, and by measuring the size by the cutting method. The prior γ particle sizes in the cases of 1 to 50 kJ/mm shown in Figure 1 are the ones obtained by this method.

[0047] On the other hand, in case of ultra-large heat input, usually, the prior γ particle size is obtained by calculating it as the prior γ particle including grain boundary ferrite since the grain boundary ferrite forms along the prior γ grain boundary, or by measuring the prior γ particle size from the microstructure obtained by being heated on a prescribed condition and then rapid-cooled using a reproduction thermal cycling test machine adjusted so that the heat input equivalent amounts are identical. The prior γ particle sizes in the cases of 100 and 150 kJ/mm shown in Figure 1 are the ones obtained from the microstructure formed by using the reproduction thermal cycling test machine, which measuring method is the latter one.

[0048] In the figure, the examples of measuring an Al deoxidized steel, a Ti added Al deoxidized steel and Mg deoxidized steels are shown and it is understood that the susceptibility of the prior γ particle size to heat input is largely varied depending on the presence of Mg oxides described in the above item 2).

[0049] That is, except the Mg deoxidized steels, the prior γ particle sizes become remarkably and obviously large as the heat input amount increases.

[0050] On the other hand, it is understood that, in case that the oxides exist in the state as specified in the above items 1) and 2) or that the oxides exist in the state as specified in the above item 2), the prior γ particle sizes vary extremely little in Mg deoxidized steels even though the heat input amounts are largely changed.

[0051] In particular, the state of the oxides as specified in the above item 2) is a factor governing the fining of the prior γ particle size.

[0052] However, if a heat input amount is up to about 60 kJ/mm, the fining of the prior γ particle size can be attained

5

even if the oxides exist only in the state as specified in the above item 1) (alone).

[0053] Moreover, even in the state of the oxides as specified in the above item 1), a pinning force functions, though the effect is small, and when the state of the oxides as specified in the above item 2) coexists therewith, the fining of the prior γ particle is markedly accelerated.

[0054] As a result of observing the steel plates having fine prior γ particles with an electron microscope, it is clarified that there exist abundantly the MIIMIII$_2$O$_4$ particles (MII: Mg, Ca, Fe, Mn, etc., MIII: Al, Ti, Cr, Mn, V, etc.) of a spinel type structure, having MgO and Mg of a face centered cubic structure in the size of 0.1 μm or less as the main constituent elements, or the complex particles of Mg contained oxides and sulfides and/or nitrides (TiN, etc.) as schematically shown in Figure 2.

[0055] In addition, by examining the relation of crystallographic orientation between the particles of Mg contained oxides and sulfides or nitrides under the observation by an electron microscope, it is also clarified that any of the particles has the relation of a completely parallel orientation.

[0056] This shows that the ultra-fine oxides of Mg act as the sites where sulfides and nitrides precipitate preferentially. That is, it is thought that the number of the nitrides effective in the pinning of crystal grains increases caused by the abundant existence of the preferential precipitation sites.

[0057] In other words, it is considered that, when heat input is small, those complex particles function as the particles effectuating pinning, and, when a retention time at a high temperature is long as in ultra-large heat input welding, though nitride particles dissolve, in the present invention, many MgO or Mg contained oxides exist and, even though the nitride particles dissolve, still existing fine oxide particles function as pinning particles at a high temperature.

[0058] Therefore, according to the present invention, the suppression of the prior γ particle growth at a HAZ, which has never been obtained in a conventional steel, can be attained.

[0059] Namely, one of the features of the present invention is, in addition to the remarkable improvement in intragranular transformation ability, to create the precipitation nuclei of nitrides by introducing oxides such as MgO, etc. finely in steel, which is dissimilar to the conventional case where the pinning of crystal grains by making use of nitrides such as TiN, etc. is intended, thereby to realize the increase of the number of nitrides, and, in case of small heat input welding where nitrides effectively function, to obtain the prior γ particles with the size of 10 to 200 μm at a HAZ due to the existence of those complex particles.

[0060] Moreover, another feature of the present invention is that, even in large or ultra-large heat input welding where nitrides dissolve and the effect of improving toughness is never obtained formerly, the prior γ particle size scarcely changes at a HAZ due to the effect of oxides alone on suppressing grain growth.

[0061] The method of adding Mg according to the present invention is, as described before, a method to add Si and Mn firstly, thereafter, either to adjust the oxygen amount in molten steel by adding Ti beforehand and thereafter to add a small amount of Mg little by little, or to add Ti and a small amount of Mg simultaneously and thereafter to finally add Mg again.

[0062] Though the optimum addition amount of Mg depends on the amount of oxygen and the like existing in molten steel after the addition of Ti, according to an experiment, since the oxygen concentration at that time depends on the addition amount of Ti and the time until Mg is added, in conclusion, no other means are required than to control the addition amounts of Ti and Mg in appropriate ranges.

[0063] Further, the final optimum amount of dissolved oxygen when Mg is added is about 0.1 to 50 ppm. The lower limit of 0.1 ppm is the lowest amount of dissolved oxygen capable of forming fine Mg oxides. On the other hand, if the dissolved oxygen exceeds 50 ppm, coarse Mg oxides form and the pinning force weakens, and for that reason, the upper limit is set at 50 ppm.

[0064] With regard to the raw material of Mg used for Mg addition and its adding method, as a result of attempting a method to add metallic Mg covered by Fe foils, a method to add Mg alloys and the like, it is clarified that, with the former method, oxidation reaction is intense when the metallic Mg is supplied in molten steel and thus the yield deteriorates. For that reason, it is preferable to add Mg alloys having relatively large specific gravity when molten steel is refined under the normal atmospheric pressure.

[0065] Hereafter explained will be the reasons why the chemical composition of the object steel is defined in the present invention.

[0066] C is a basic element for enhancing the strength of a base steel. An addition amount of 0.01% or more is required for securing the enhancement effect. But, if it is excessively added in excess of 0.2%, weldability and toughness of a steel deteriorate, and therefore the upper limit is set at 0.2%.

[0067] Si is an indispensable element used as a deoxidizing element in steelmaking and an addition of 0.02% or more into a steel is required. However, if it is added in excess of 0.5%, HAZ toughness deteriorates, and therefore the upper limit is set at 0.5%.

[0068] Mn is an indispensable element for securing the strength and toughness of a base steel. However, if it is added in excess of 2%, HAZ toughness deteriorates markedly, but in contrast, with the addition of less than 0.3%, the strength of a base steel is hardly secured. Therefore, the addition amount is limited in the range of 0.3 to 2%.

[0069] P is an element affecting the toughness of a steel. Since the toughness of not only a base steel but also a HAZ deteriorates greatly with a content exceeding 0.03%, the upper limit is set at 0.03%.

[0070] S forms coarse sulfides, and thus deteriorates toughness if it is added in excess of 0.03%, but, with a content of less than 0.0001%, the amount of formed sulfides such as MnS, etc., which are effective in the generation of intragranular ferrite, lowers greatly. Therefore, the range of the addition amount is set at 0.0001 to 0.03%.

[0071] Al is usually added as a deoxidizing agent. In the present invention, the upper limit of Al is set at 0.05% since its addition in excess of 0.05% hinders the effect of Mg addition, and its lower limit is set at 0.0005% since Al addition of at least 0.0005% is required for forming MlIMlIl$_2$O$_4$ stably.

[0072] Ti is an element effective in the fining of crystal grains, acting as a deoxidizing agent and further an element to form nitrides. However, a large amount of its addition causes the considerable deterioration of toughness due to the formation of carbides and therefore the upper limit has to be 0.05%. Then, since the addition amount of at least 0.003% is required for securing a desired effect, the range of the addition amount is set at 0.003 to 0.05%.

[0073] Mg is a main alloying element in the present invention and is added as a deoxidizing agent mainly. However, if it is added in excess of 0.01%, coarse oxides tend to form and the toughness of a base steel and a HAZ deteriorates. On the other hand, with the addition amount of less than 0.0001%, the formation of oxides which are required for intragranular transformation and as pinning particles cannot be sufficiently expected. Therefore, the range of the addition amount is set at 0.0001 to 0.010%.

[0074] O (oxygen) is an essential element to form Mg contained oxides. If the oxygen amount finally remaining in a steel is less than 0.0001%, the number of oxides is insufficient, and therefore the lower limit is set at 0.0001%. On the other hand, if the amount of remaining oxygen exceeds 0.008%, coarse oxides increase and the toughness of a base steel and a HAZ deteriorates, and therefore the upper limit is set at 0.008%.

[0075] Further, in the present invention, one or more elements of Cu, Ni, Cr, Mo, V, Nb, Zr, Ta and B may be added as the elements which enhance strength and toughness.

[0076] Cu is an effective element in enhancing strength without deteriorating toughness. However, with the amount of less than 0.05%, the effect does not appear, but, with the amount exceeding 1.5%, cracks tend to occur during the heating of a slab or welding. Therefore, the range of the content is set at 0.05 to 1.5%.

[0077] Ni is an effective element in enhancing toughness and strength, and, to secure the effect, an addition amount of 0.05% or more is required. However, when the addition amount exceeds 5%, weldability deteriorates, and therefore the upper limit is set at 5%.

[0078] Cr is added in the amount of 0.02% or more for effectively enhancing the strength of a steel by precipitation hardening, but a large amount of its addition exceeding 1.5% raises hardenability, generates a bainite structure and deteriorates toughness. Therefore, the upper limit is set at 1.5%.

[0079] Mo is an element which enhances hardenability and, at the same time, improves strength by forming carbonitrides. The addition amount of 0.02% or more is required for securing the effect, but the addition in large amount exceeding 1.5% enhances strength excessively and deteriorates toughness considerably. Therefore, the range of the content is set at 0.02 to 1.5%.

[0080] V is an element which forms carbides and nitrides and is effective in enhancing strength, but the effect cannot be secured with the addition amount of less than 0.01% and, in contrast with this, toughness deteriorates with the addition amount of exceeding 0.1%. Therefore, the range of the content is set at 0.01 to 0.1%.

[0081] Nb is an element which forms carbides and nitrides and is effective in enhancing strength, but the effect cannot be secured with the addition amount of less than 0.0001% and toughness deteriorates with the addition amount of exceeding 0.2%. Therefore, the range of the content is set at 0.0001 to 0.2%.

[0082] Each of Zr and Ta is, like Nb, an element which forms carbides and nitrides and is effective in enhancing strength, but the effect cannot be secured with the addition amount of less than 0.0001% and, in contrast with this, toughness deteriorates with the addition amount of exceeding 0.05%. Therefore, the range of the content is set at 0.0001 to 0.05%.

[0083] B generally enhances hardenability when it is in the state of solid solution and is an element which decreases N in solid solution by forming BN and enhances the toughness of a weld heat-affected zone. The above effects can be secured with the addition of 0.0003% or more, but its excessive addition causes the deterioration of toughness and therefore the upper limit is set at 0.005%.

[0084] Ca and REM suppress the generation of elongated MnS by forming sulfides and improve the properties in the plate thickness direction of a steel material, particularly a lamellar tear property. Each of Ca and REM cannot secure those effects with the addition of less than 0.0005% and therefore the lower limit is set at 0.0005%. In contrast with this, with the addition exceeding 0.005%, the number of the oxides of Ca and REM increases and the number of ultrafine Mg contained oxides decreases. Therefore, the upper limit is set at 0.005%.

[0085] A steel containing above-mentioned components is refined in a steelmaking process, continuous casting, the heavy plate thus produced is heated and rolled. In this case, with regard to a rolling method, a heating and cooling method and a heat treatment method, even though methods conventionally applied in the relevant fields are adopted,

there is no affection to HAZ toughness at all.

[0086] In particular, based on the fact that the smaller the grain size of a base steel is, the larger the grain size and the difference thereof at a HAZ are, the fining of a prior γ grain size at a HAZ according to the present invention demonstrates a large effect even in the case that not only HAZ toughness but also hardness matching, etc. have to be taken into consideration.

Examples

[0087] Examples according to the present invention will be described hereunder.

[0088] Steel ingots having the chemical compositions shown in Tables 1 and 2 (continued from Table 1) were subjected to hot rolling and heat treatment and produced into steel plates, and thereafter the steel plates were welded with the small weld heat input of 1.7 kJ/mm, the large weld heat input of 20 kJ/mm and the ultra-large weld heat input of 150 kJ/mm. Then, prior γ grain sizes at HAZs were measured with the aforementioned cutting method and the susceptibility of HAZ toughness (test pieces were taken from the region of the coarsest grains) to heat inputs was evaluated by the Charpy impact test. The results are shown in Table 3.

[0089] Note that ΔvEo in Table 3 is obtained by calculating the difference of Charpy absorbed energy between the cases of small heat input (1.7 kJ/mm) and ultra-large heat input (150 kJ/mm), that is, [toughness in case of small heat input: vEo (J)] - [toughness in case of ultra-large heat input: vEo (J)], and each absorbed energy is an average of the values obtained by the measurement of three test pieces at 0°C.

[0090] Further note that, with regard to $\lambda 1$ and $\lambda 2$, $\lambda 1$ and $\lambda 2$ are average particle intervals of oxides calculated from ten photographs taken with an electron microscope in the magnification of 1,000 times for $\lambda 1$ and 100,000 times for $\lambda 2$.

Table 1 (continue to Table 2)

Steel		C	Si	Mn	P	S	Al	Ti	Mg	O	Cu	Ni	Cr
1		0.05	0.10	1.21	0.005	0.0030	0.0040	0.005	0.0033	0.0042	0.40	0.30	
2		0.15	0.13	1.32	0.008	0.0053	0.0030	0.003	0.0041	0.0008			
3		0.10	0.08	1.50	0.003	0.0044	0.0084	0.012	0.0003	0.0032			
4		0.14	0.07	1.60	0.004	0.0035	0.0005	0.016	0.0019	0.0025			
5		0.15	0.25	1.47	0.009	0.0053	0.0071	0.012	0.0019	0.0024		0.15	
6		0.18	0.10	0.70	0.026	0.0029	0.0061	0.012	0.0025	0.0033			
7		0.19	0.02	0.31	0.003	0.0228	0.0053	0.013	0.0008	0.0028		0.05	
8		0.13	0.15	1.27	0.007	0.0051	0.0026	0.008	0.0028	0.0025			
9		0.09	0.17	1.90	0.005	0.0002	0.0134	0.010	0.0095	0.0074	0.20	0.10	
10		0.07	0.20	1.54	0.008	0.0041	0.0042	0.041	0.0098	0.0079	0.30	0.15	
11	Invent-	0.09	0.22	1.48	0.002	0.0032	0.0041	0.024	0.0042	0.0022			
12	ed	0.11	0.25	1.35	0.004	0.0026	0.0051	0.012	0.0033	0.0035		0.15	
13	steel	0.12	0.31	1.21	0.006	0.0105	0.0042	0.024	0.0041	0.0032		0.05	
14		0.13	0.09	1.35	0.006	0.0031	0.0008	0.013	0.0043	0.0005			
15		0.06	0.28	1.05	0.004	0.0033	0.0061	0.012	0.0079	0.0078		0.25	
16		0.05	0.32	1.21	0.003	0.0031	0.0058	0.008	0.0082	0.0052	0.40	0.80	1.30
17		0.06	0.48	1.35	0.002	0.0042	0.0032	0.010	0.0020	0.0055	0.05		
18		0.14	0.24	1.45	0.004	0.0053	0.0029	0.005	0.0028	0.0047			
19		0.12	0.28	1.33	0.017	0.0029	0.0063	0.047	0.0001	0.0023		4.50	0.10
20		0.01	0.12	0.90	0.003	0.0041	0.0221	0.012	0.0015	0.0014	1.00	3.00	
20-2		0.01	0.12	0.90	0.003	0.0041	0.0221	0.012	0.0010	0.0014	1.00	3.00	
21		0.08	0.31	1.09	0.002	0.0029	0.0032	0.017	0.0073	0.0078	0.05		
21-2		0.08	0.31	1.09	0.002	0.0029	0.0032	0.017	0.0050	0.0078	0.05		
22		0.08	0.31	1.20	0.004	0.0025	0.0453	0.018	0.0054	0.0032			
23		0.25	0.18	1.54	0.005	0.0175	0.0052	0.012	0.0019	0.0027	1.60		
24		0.17	0.65	1.34	0.007	0.0065	0.0006	0.013	0.0038	0.0020			
25		0.14	0.12	2.40	0.015	0.0033	0.0072	0.008	0.0028	0.0070			
26		0.12	0.25	1.11	0.040	0.0045	0.0087	0.019	0.0031	0.0008	0.015		0.15
27		0.15	0.17	0.95	0.003	0.0351	0.0053	0.017	0.0005	0.0020			
28	Compar-	0.17	0.03	0.50	0.002	0.0032	0.0004	0.010	0.0009	0.0015		0.33	
29	ative	0.18	0.05	1.02	0.005	0.0031	0.0543	0.023	0.0083	0.0023			
30	steel	0.09	0.09	0.60	0.003	0.0235	0.0032	0.064	0.0034	0.0033		5.50	
31		0.07	0.12	0.90	0.024	0.0022	0.0041	0.002	0.0043	0.0027	0.40	0.13	1.60
32		0.18	0.05	0.45	0.002	0.0015	0.0061	0.010	<0.0001	0.0009			
33		0.16	0.22	0.78	0.004	0.0081	0.0043	0.008	0.0228	0.0072			
34		0.05	0.41	1.79	0.003	0.0051	0.0052	0.045	0.0139	0.0090	0.10	0.14	
35		0.07	0.35	1.57	0.002	0.0035	0.0049	0.012	0.0119	0.0001	0.30	0.45	

Table 2 (continue from Table 1)

Steel	(kgf)	Chemical composition (mass%)								Composition requirement of the present invention
		Mo	V	Nb	Zr	Ta	B	Ca	REM	
1				0.1380				0.0020		O
2								0.0012		O
3		0.30	0.04			0.0004			0.0008	O
4					0.0051					O
5				0.0120		0.0032	0.0006			O
6				0.0012				0.0021	0.0035	O
7		0.03						0.0011		O
8				0.0009				0.0022		O
9		0.05					0.0008			O
10			0.07			0.0300		0.0024		O
11			0.06	0.1100					0.0042	O
12 Invented steel					0.0137					O
13			0.09	0.0025						O
14								0.0035	0.0023	O
15		0.10		0.0123			0.0010			O
16		0.18		0.0060			0.0005		0.0007	Regular
17				0.0008		0.0132				rolling and
18		1.20				0.0229		0.0011		air cooling O
19				0.0128		0.0420		0.0006	0.0006	O
20		0.20	0.05	0.0239			0.0045	0.0017	0.0015	O
20-2		0.20	0.05	0.0239			0.0045	0.0017	0.0015	O
21		0.80	0.05		0.0400	0.0024	0.0003			O
21-2		0.80	0.05		0.0400		0.0003			O
22				0.1500				0.0021		O
23			0.05	0.0080						O
24		1.70	0.20			0.0040	0.0015	0.0013		X
25				0.0135				0.0012		X
26		0.20	0.06		0.0030	0.0100		0.0060		X
27				0.0213				0.0017	0.0006	X
28 Comparative steel		0.30				0.0050				X
29			0.08		0.0210		0.0060		0.0013	X
30				0.3120			0.0005	0.0017		X
31		0.25		0.0138			0.0021			X
32						0.0080			0.0007	X
33				0.0062						X
34		0.30	0.02	0.0550			0.0008		0.0055	X
35			0.04			0.0585		0.0021		X

Table 3

		Production method	Plate thickness (mm)	d1 (µm)	d2 (µm)	d3 (µm)	λ1 (µm)	λ2 (µm)	vEo (kgf·m)	ΔvEo (kgf·m)
1		Controlled rolling and controlled cooling	40	35	60	100	60	8.3	15.0	2.0
2		Regular rolling and air cooling	40	40	60	100	55	8.2	16.0	2.5
3		Regular rolling and air cooling	250	65	80	140	75	9.3	18.0	3.1

EP 1 143 023 A1

Table 3 (continued)

		Production method	Plate thickness (mm)	d1 (μm)	d2 (μm)	d3 (μm)	λ1 (μm)	λ2 (μm)	vEo (kgf·m)	ΔvEo (kgf·m)
4		Controlled rolling and controlled cooling	60	45	50	120	65	9.0	22.0	3.0
5		Controlled rolling and controlled cooling	50	30	60	80	45	7.0	24.0	-2.5
6		Controlled rolling and controlled cooling	50	60	70	90	50	7.5	20.5	-2.3
7		Regular rolling and air cooling	150	80	140	170	95	15.0	11.0	-2.2
8		Controlled rolling and controlled cooling	40	70	100	140	68	9.5	14.0	3.8
9		Controlled rolling and controlled cooling	120	20	40	45	35	2.0	25.3	3.9
10		Controlled rolling and controlled cooling	40	10	15	20	30	1.0	28.0	2.4
11	Invented steel	Direct quenching and tempering	50	80	85	105	54	8.5	20.0	2.3
12		Direct quenching and tempering	60	55	70	120	50	9.3	16.0	2.1
13		Controlled rolling and controlled cooling	30	65	90	140	68	9.5	17.0	-2.0
14		Controlled rolling and controlled cooling	15	90	105	120	60	9.2	18.0	3.5
15		Quenching and tempering	60	35	55	70	45	5.0	26.0	2.0
16		Controlled rolling and controlled cooling	60	40	60	80	52	6.3	24.0	3.8

Table 3 (continued)

		Production method	Plate thickness (mm)	d1 (μm)	d2 (μm)	d3 (μm)	λ1 (μm)	λ2 (μm)	vEo (kgf·m)	ΔvEo (kgf·m)
17	5.9	Quenching and tempering	80	75	95	135	72	7.0	14.5	1.9
18		Controlled rolling and controlled cooling	60	80	95	140	85	7.5	18.0	3.3
19	5.2	Controlled rolling and controlled cooling	60	95	140	185	98	22.0	10.2	2.7
20		Direct quenching and tempering	100	70	110	125	63	9.3	19.5	2.6
20-2	10.3	Direct quenching and tempering	100	70	125	150	150	9.3	15.5	3.6
21	0.3	Direct quenching and tempering	80	15	35	50	35	3.0	23.3	2.1
21-2	0.3	Direct quenching and tempering	80	85	140	190	38	35.0	20.3	3.1
22	2.2	Controlled rolling and controlled cooling	40	75	95	145	75	9.8	10.6	-1.7
23		Regular rolling and air cooling	40	80	120	145	80	7.4	8.8	6.4
24		Controlled rolling and controlled cooling	40	90	140	160	85	7.8	3.8	2.5
25		Controlled rolling and controlled cooling	40	60	90	110	55	5.4	2.5	2.1
26		Direct quenching and tempering	60	70	95	120	59	5.2	2.0	0.02
27		Controlled rolling and controlled cooling	50	95	140	180	90	8.6	2.4	1.0

Table 3 (continued)

		Production method	Plate thickness (mm)	d1 (µm)	d2 (µm)	d3 (µm)	λ1 (µm)	λ2 (µm)	vEo (kgf·m)	ΔvEo (kgf·m)
28		Controlled rolling and controlled cooling	50	100	360	595	320	75.0	7.6	5.6
		Quenching and tempering								
30	comparative steel	Regular rolling and air cooling	120	55	95	130	66	6.8	7.9	5.2
31		Controlled rolling and controlled cooling	40	95	230	355	200	80.0	5.3	3.3
32		Direct quenching and tempering	80	120	400	500	300	110.0	16.0	10.3
33		Regular rolling and air cooling	50	50	70	80	40	4.0	2.7	0.3
34		Controlled rolling and controlled cooling	60	45	60	75	35	3.6	3.3	0.3
35		Regular rolling and air cooling	40	110	150	298	120	50.4	4.2	2.2
36		Controlled rolling and controlled cooling	40	120	170	420	185	100.0	13.0	11.0
37		Regular rolling and air cooling	80	135	180	440	190	120.0	12.0	10.5

d1: prior γ grain size at the heat input of 1.7 kJ/mm
d2: prior γ grain size at the heat input of 20.0 kJ/mm
d3: prior γ grain size at the heat input of 150.0 kJ/mm (note that d3 of the steel 20-2 is the prior γ grain size at the heat input of 60.0 kJ/mm)
λ1: average particle interval of Mg contained oxides (0.2 to 5.0 µm)
λ2: average particle interval of Mg contained oxides (0.005 to 0.2 µm)
vEo (kgf·m): Charpy absorbed energy at 0°C in case of the heat input of 1.7 kJ/mm
ΔEo (kgf·m): [Charpy absorbed energy at the heat input of 1.7 kJ/mm] - [Charpy absorbed energy the heat input of 150.0 kJ/mm (or 60.0 kJ/mm)]

[0091] The steels 1 to 22 show the examples according to the present invention. As is clear from Table 3, the prior γ grain sizes of these invented steels are all 200 µm or less in the wide heat input range from small heat input to ultra-large heat input. Though the steels 20-2 and 21-2 have almost the same chemical compositions as those of the steels

20 and 21, respectively, the deoxidizing conditions are varied and the Mg amounts are somewhat different. Though λ1 in case of the steel 20-2 and λ2 in case of the steel 21-2 are outside the range specified in the present invention, even in these cases, it is observed that the grain size of the steel 20-2 scarcely changes and it is understood that the grain size of the steel 21-2 is 200 μm or less at the heat input condition of 60.0 kJ/mm. Further, Charpy absorbed energy of all those invented steels exceeds 10 kgf-m and it shows that the above invented steels have high toughness.

[0092] Moreover, the difference of Charpy absorbed energy between the cases of small heat input and ultra-large heat input is as small as 4 kgf-m at the largest and HAZ toughness does not vary even on the wide-ranging heat input conditions.

[0093] Note that there are cases where minus symbols are placed on the values of the aforementioned Charpy absorbed energy differences and that shows the toughness is improved in spite that the prior γ grain sizes become large. This results from the fact that the intragranular transformation ability of Mg contained oxides is extremely large according to the present invention.

[0094] On the other hand, the steels 23 to 35 are the comparative steels produced on other conditions than that specified in the present invention. More specifically, the comparative steels 23, 24, 25, 26, 27, 29, 30, 33, 34 and 35 are the cases where at least one of the basic components or the selective elements is added in the amount outside the composition range specified in the present invention.

[0095] In the aforementioned comparative steels, though the average grain intervals of oxides, which are an important requirement in the present invention, mostly satisfy the requirements specified in the present invention, elements causing toughness deterioration are added in excess and that results in accelerating the deterioration of HAZ toughness when the steels are welded on small heat input conditions and ultra-large heat input conditions.

[0096] Comparative steels 28 and 31 are the cases where the amounts of Al and Ti are lower than their lower limits specified in the present invention, respectively. In these cases, prior γ grain sizes coarsen as the heat input increases and thus the both comparative steels have poor toughness.

[0097] Comparative steel 32 has no Mg addition, and under a small heat input condition, has good toughness. But under an ultra-large heat input condition, the steel has considerable deterioration of toughness and, consequently, the large Charpy absorbed energy difference of 10.3 kgf-m.

[0098] All of the comparative steels mentioned above have low HAZ toughness, and moreover the HAZ toughness further deteriorates when heat input amount is high.

[0099] Comparative steels 33 and 34 have many fine oxides and, because of that, have largely deteriorated toughness even though the prior γ grain sizes are sufficiently small compared with other cases.

[0100] The reason is that coarse particles of 5 μm or more are mainly generated caused by the addition of an excessive amount of Mg or O and then brittle fracture is accelerated.

[0101] Comparative steels 36 and 37 are the cases where their chemical compositions are the same as those of the invented steels 1 and 2, respectively, but the amounts of oxygen dissolved in molten steel exceed 50 ppm when the prescribed amounts of Mg are added at the final stage.

[0102] After all, in comparative steels 36 and 37, ultra-fine oxides are not generated sufficiently in the steels and therefore the coarsening of prior γ grains and the considerable deterioration of toughness occur.

Industrial Applicability

[0103] According to the chemical compositions and the production method specified in the present invention, the growth of prior γ grains at a HAZ can be suppressed, while disregarding heat input conditions, by either adding a prescribed amount of Mg properly after adding Ti or adding a prescribed amount of Mg properly after adding Ti and Mg simultaneously.

[0104] In the present invention, it is possible to enhance HAZ toughness over wide-ranging heat input conditions by the suppression effect.

[0105] As a result, in various technical fields including offshore structures, line pipes for transporting natural gas or crude oil, architecture, shipbuilding, bridges and construction equipment, safety against brittle fractures of welded structures is remarkably improved.

[0106] The present invention can, accordingly, greatly contribute to the development of various industrial technologies.

Claims

1. A steel for a welded structure with HAZ toughness not susceptible to heat input, **characterized by**: containing, in terms of wt%,

EP 1 143 023 A1

C: 0.01 to 0.2%,
Si: 0.02 to 0.5%,
Mn: 0.3 to 2%,
P: 0.03% or less,
S: 0.0001 to 0.03%,
Al: 0.0005 to 0.05%,
Ti: 0.003 to 0.05%,
Mg: 0.0001 to 0.01%, and
O: 0.0001 to 0.008%,

with the balance consisting of Fe and unavoidable impurities;
and having particles dispersed in the steel at an average particle interval of 30 to 100 µm, the particles being formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle sizes of 0.2 to 5 µm as their nuclei, or particles dispersed in the steel at an average particle interval of 30 µm or less, the particles being formed by precipitating either any one of sulfides and nitrides singly or the both thereof in combination using Mg contained oxides with the particle sizes of 0.005 to less than 0.2 µm as their nuclei.

2. A steel for a welded structure with HAZ toughness not susceptible to heat input according to claim 1, **characterized by** further containing, in terms of wt%, one or more of

Cu: 0.05 to 1.5%,
Ni: 0.02 to 5%,
Cr: 0.02 to 1.5%,
Mo: 0.02 to 1.5%,
V: 0.01 to 0.1%,
Nb: 0.0001 to 0.2%,
Zr: 0.0001 to 0.05%,
Ta: 0.0001 to 0.05%, and
B: 0.0003 to 0.005%.

3. A steel for a welded structure with HAZ toughness not susceptible to heat input according to claim 1 or 2, **characterized by** further containing, in terms of wt%, one or more of

Ca: 0.0005 to 0.005% and
REM: 0.0005 to 0.005%.

4. A steel for a welded structure with HAZ toughness not susceptible to heat input according to any one of claims 1 to 3, **characterized by** having the prior austenite grain sizes of 10 to 200 µm in its HAZ structure without depending on weld heat input.

5. A method for producing a steel for a welded structure with HAZ toughness insusceptible to heat input according to any one of claims 1 to 4, **characterized by**: casting the steel in the state of adjusting the dissolved oxygen amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and a required amount of Mg successively or simultaneously after carrying out a weak deoxidation treatment by adding Si and Mn at a steelmaking process; or casting the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less.

6. A method for producing a steel for a welded structure with HAZ toughness insusceptible to heat input according to any one of claims 1 to 4, **characterized by**: casting the steel in the state of adjusting the dissolved oxygen amount at 50 ppm or less by adding 0.003 to 0.05 wt% of Ti and required amounts of Al, Ca and Mg successively or simultaneously after carrying out a weak deoxidation treatment by adding Si and Mn at a steelmaking process; or casting the steel after further adding Mg so that the final content of Mg is 0.01 wt% or less.

Fig.1

Fig.2

Fig.2

⬤ : Mg contained oxide

Nitride

Sulfide
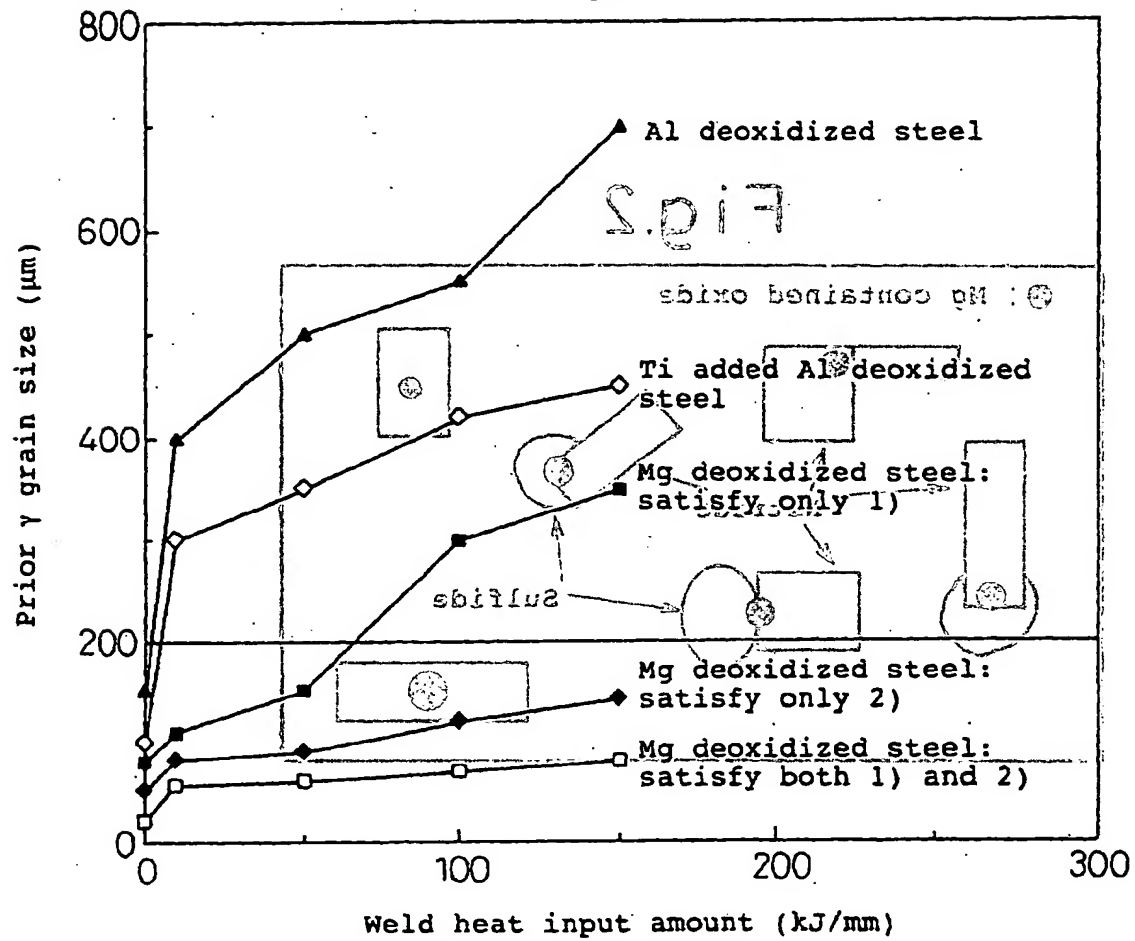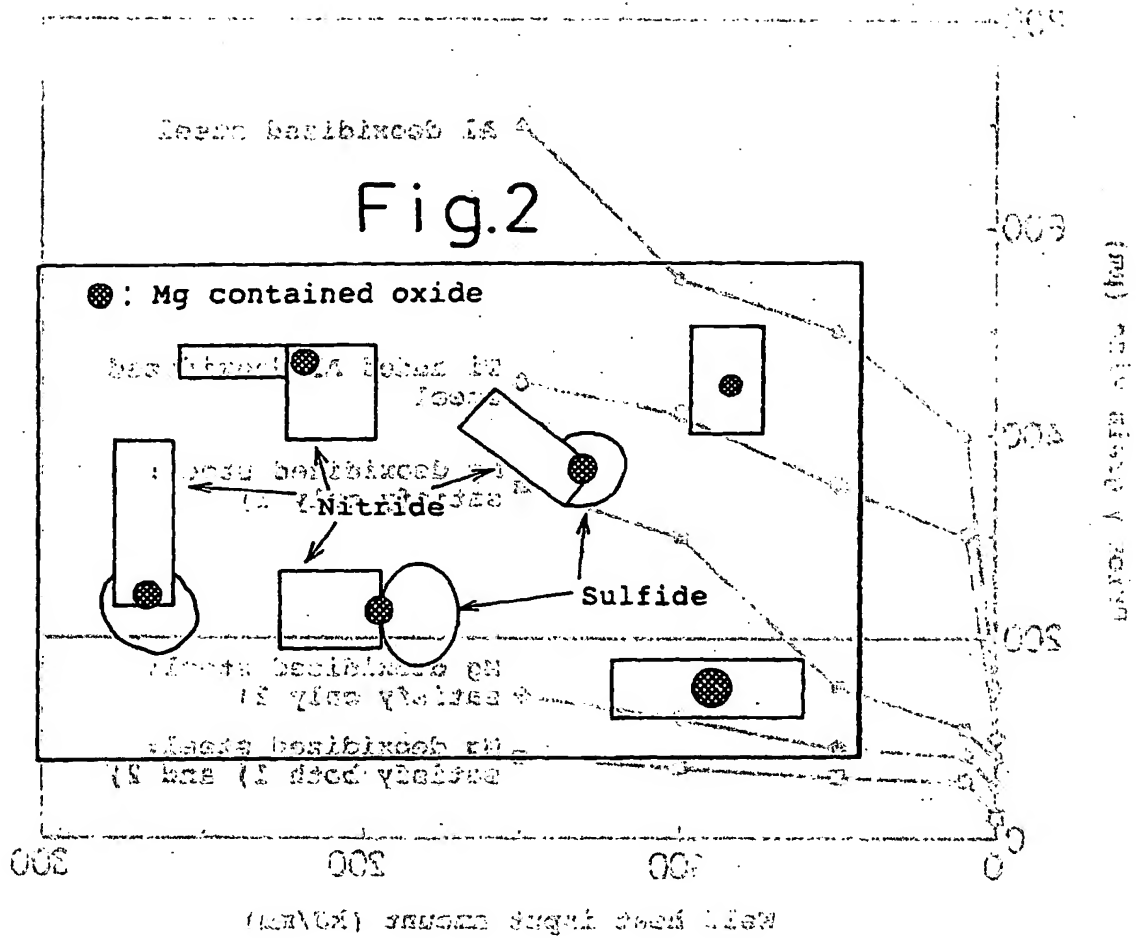
INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/07091

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C22C38/00, C21C7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 C22C38/00-38/60, 33/04, C21C7/00-7/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Jitsuyo Shinan Toroku Koho	1996-2000
Kokai Jitsuyo Shinan Koho	1971-2000	Toroku Jitsuyo Shinan Koho	1994-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	JP, 11-293382, A (Nippon Steel Corporation 社), 26 October, 1999 (26.10.99), Claims; column 4, lines 39-41 (Family: none)	1-6
X	JP, 9-310147, A (Nippon Steel Corporation), 02 December, 1997 (02.12.97), Claims (Family: none)	1-6
X	JP, 10-298705, A (Nippon Steel Corporation), 10 November, 1998 (10.11.98), Claims (Family: none)	1-6
X	JP, 5-43977, A (Nippon Steel Corporation), 23 February, 1993 (23.02.93), Claims (Family: none)	1-6
X	JP, 11-21613, A (Nippon Steel Corporation), 26 January, 1999 (26.01.99), Claims (Family: none)	1-6

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 December, 2000 (08.12.00)	19 December, 2000 (19.12.00)

Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)